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TITLE: Laser Fabrication and Characterization of Adhesive-Free Joints for Encapsulation of Biomedical Implant Devices

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TITLE: Materials Research Society Symposium Proceedings. Volume 845, 2005. Nanoscale Materials Science in Biology and Medicine, Held in Boston, MA on 28 November-2 December 2004

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Laser Fabrication and Characterization of Adhesive-Free Joints For Encapsulation of Biomedical Implant Devices

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ABSTRACT

Laser-fabricated joints of sub-millimeter widths between biocompatible, dissimilar materials have the potential for applications as encapsulation of miniature implant biomedical devices. In this work, we briefly describe the laser joining method of a very promising system, polyimide/titanium-coated borosilicate glass, and present and discuss results from characterization of such laser joints by means of mechanical failure (tensile) tests, optical microscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Our results suggest the formation of strong chemical bonds between Ti-containing species and certain polymeric functional groups. Mechanical tensile strength failure test showed that such joint experience only limited, disappearing with time degradation as a result of soaking in physiological solutions.

INTRODUCTION

The design of the encapsulation of advanced medical implants, such as devices that electrically stimulate and / or record neural activity, poses a number of serious requirements to the materials that are used. Among these requirements, biocompatibility and long-term stability are crucial. Often, the functionality of such devices requires the employment of dissimilar materials for which there is no reliable ways of joining that would also satisfy the need for biocompatibility and stability. Poor biocompatibility and lack of long-term stability, high heat input during soldering, and adhesive shrinkage during cure are indeed among the major drawbacks of the existing joining techniques. Such limitations can be overcome by laser joining techniques that intrinsically provide excellent focusing to spot sizes in the micrometer range, combined with precise control of the laser power in the focal spot to enable highly localized processing with minimum heat effect outside the joint region.

Recently we studied the nature of polyimide/bulk-Ti laser-fabricated joints, which were made in ambient conditions and our results gave evidence for a very sharp interface based on the creation of chemical bonds between Ti and O and C contained in polyimide [1]. Reactive metals like Ti are known to have low mobility in polymers and to form relatively sharp interfaces with them [2,3]. Titanium is believed to interact primarily with the oxygen double bonded to carbon in the carbonyl groups $>C=O$, which form part of the PI molecular chains, and to form bonding configurations of the type Ti-O-C. XPS results have given evidence for the existence of TiO_2 particles [4] and Ti-C [5] bonds at such interfaces (obtained and examined under clean, vacuum conditions), and theoretical ab initio self-consistent-field calculations have identified chemical sites along the PI chains and mechanisms that favor the formation of such bonds [6]. According

to our results, laser heating in ambient conditions also provides a mechanism for formation of joints based on strong chemical bonding between the surfaces of the Ti foil and the PI sheet.

The feasibility of laser joining PI to titanium and PI to titanium-coated glass has been investigated, and ranges of processing parameters that permit successful joining have been identified [7]. In order to understand the influence of the laser fabrication conditions on the joint quality and stability, we examined laser–fabricated joints between PI and titanium-coated borosilicate glass (BSG) in tensile mechanical failure tests and by optical microscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Such laser joints were also exposed to (soaked in) artificial cerebrospinal fluid (CSF) from Harvard Apparatus for different periods of time at 37 °C in order to study any degradation effects caused by such physiological solutions.

SAMPLES PREPARATION AND EXPERIMENTAL CONDITIONS

PI sheet (Imidex, Westlake Plastics Company) was laser-joined to BSG coated with 0.2μm-thick, sputtered Ti film (Pyrex 7740, Corning) by means of continuous wave radiation from a Yb-doped fiber at $\lambda = 1.1\mu$m. A transmission joining configuration [7] was used in which a clamping pressure of 200 MPa was used for the fabrication of the samples examined in this work. The laser beam with a total power of 1.0 W was loosely focused on the Ti surface to a spot with diameter of 300μm. A scanning speed of 100mm/min was used to produce the joint line. PI is known to be transparent in the near-infrared region, and the PI sheet that we used was characterized by spectrophotometry and found to have a transmittance of 81% at $\lambda = 1.1\mu$m.

Samples of the type described above with densely arranged parallel joint lines were also prepared for XPS measurements. These were separated into their PI and Ti parts by peeling in air and immediately introduced in the UHV analysis chamber of a Perkin Elmer model 5500 XPS spectrometer. Both sides of the joint were studied. A relatively large analysis area was used that averaged over several joint lines and inter-joint regions following the procedure outlined in [1]. This approach was found to provide a good signal-to-noise ratio, and it insured that the signal was originating from a known area of the peeled joint. Thus all spectra that were obtained contained a ~50% contribution from the non-laser-treated surface of the sample, and the spectral analysis needed to take this into account. The base vacuum pressure was 5×10^{-10}Torr and an Ar-ion beam was used to sputter the sample surfaces in order to obtain spectra from various depths below the surface. A low-energy electron beam (neutralizer) was used to compensate for charging effects when studying the PI sheet (not needed in studying the Ti-coated glass plate).

Both the as-received and CSF-soaked laser joint samples were tested for mechanical tensile strengths of failure. The testing equipment used in this case consisted of a 6-axis micro-tester, which is a general-purpose micromechanical/thermal testing instrument. The machine was fully controlled by a computer, and could be operated both in displacement and load controls with six degrees of freedom [8], i.e., three orthogonal translations and three rotations. The displacement resolution of each closed-loop, DC-motor-drive stage was maintained at 0.1 μm in translations and 0.001 degree in rotations. A capacitance gage measured the displacement of the sample.

Micro-Raman spectroscopy measurements were performed on laser-joint samples that were subjected to tensile mechanical testing and separated into their PI and glass parts. These experiments were done on a Renishaw InVia Raman microscope equipped with an Ar-ion laser emitting at λ=514.5nm. A 50X microscope objective was used to both deliver the excitation light and collect the Raman scattering signal (in a backscattering set-up), providing a spatial resolution of about 3μm. The machine was fully controlled by a PC and was also equipped with a

motorized high-precision XYZ microscope stage and a digital video camera allowing full control and documentation of the location from which the spectra were being collected.

RESULTS AND DISCUSSION

Tensile mechanical test results

The tensile mechanical test samples' configuration and sizes are shown in Figure 1a below. Upon testing, samples were subjected to uniaxial tension (in-plane) by turning on the motor that moves in direction perpendicular to the laser joint. The software that controls the machine also acquires load cell and capacitance gage information (load-displacement data). The failure loads obtained for all samples were normalized by the corresponding, measured bond lengths to account for any joint length variations. The test results are summarized in Figure 1b. Between 6 and 10 samples per data point were used to obtain statistically reliable averages. As can be seen in this figure, the joint strength decreases during the first 2 – 4 weeks of exposure to CSF and then stabilizes at values that are about half as high as those of the as-received samples. Despite this reduction in strength, the joints retain considerably high and stable strength values after such a long-term exposure to CSF.

Inspection of the failed joints under an optical microscope showed that the as-received samples (i.e. with no CSF treatment) failure occurred almost entirely within the glass. On the other hand the CSF-soaked samples showed a mixed mode of failure that included both the glass and the PI, with the fraction of the PI failure somewhat increasing with the soak time. Apparently, the joint degradation mechanism is primarily due to CSF-induced weakening of the PI (and not the glass) in the joint region.

XPS results

Both non-treated and 14-days-CSF-saoked (at 37°C) samples were studied. There were no significant differences between the XPS spectra of the CSF-soaked and the non-treated samples. Apparently, the information that XPS can provide is not specific enough to reveal changes
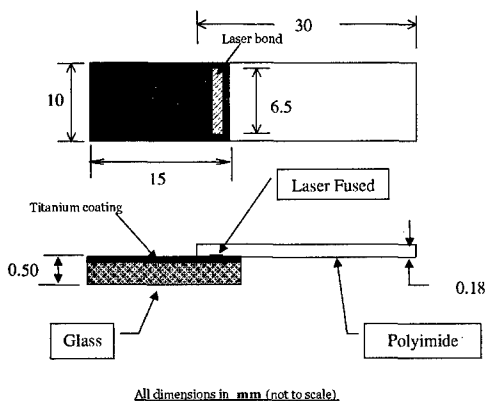

Figure 1a. Mechanical test sample configuration and sizes.
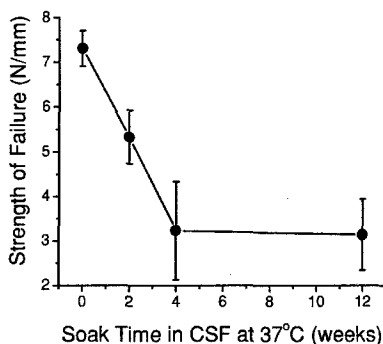
Figure 1b. Strength of failure as a function of CSF soak time (at 37°C).

related to the mild joint degradation that resulted from this short-term (14 days) exposure to CSF and was otherwise evident from the mechanical tensile tests described above. However, we do not exclude the possibility that the XPS technique be useful in studying longer-term CSF-treated samples (say, 3-month), where the degradation effects would be more pronounced. We have not been able to study such longer-term CSF-treatment cases, but our XPS results provide important information about the structure of the PI/Ti interfaces that formed as result of the laser irradiation and heating during the joint fabrication process.

These interfaces can be expected to be similar or identical to those that form when laser-joining PI to bulk Ti plates [1]. Indeed that is what we observe and the XPS lineshapes of *the glass side* of a sample after peeling are shown below in Figures 2a and 2b. In both the CSF-soaked and the non-soaked sample cases *the PI side* did not contain any Ti which means that upon peeling the sample fails entirely within the PI plate (unlike the case of tensile testing failure described above section where the samples fail either entirely or in part in the glass substrate). Apparently, the mode of failure upon peeling is different from the one when tensile mechanical failure tests are preformed. In Figure 2a is shown the XPS C 1s line high-resolution (multiplex, Shirley baseline subtracted) spectrum as a function of depth of sputtering (i.e. sputtering time). At the surface (0s sputtering, bottom), the spectrum corresponds to one from a PI surface with contributions from carbonyl groups (close to 288eV) and other types of C environments that form the PI polymeric molecular structure. Upon sputtering the carbonyl group line disappears, the intensity (both total and relative to each other) of the other contribution changes, and, most significantly a new line at around 281eV, associated with Ti-C bonds, appears and becomes stronger (see especially the spectrum at 1200s of sputtering).

The Ti 2p XPS spectra are shown in Figure 2b. The spectra taken from the surface correspond to fully oxidized Ti, i.e. TiO_2. Deeply in the substrate, after 1200s of sputtering (corresponding to a depth of 40-50nm) the spectra consist almost entirely of pure, metalic Ti: the 2p doublet is shifted downward by about 6eV. Between these two extreme cases we observe a mixture of states that evolve from pure oxide to pure metal with the increase of the sputtering time. These intermediate chemical states can be interpreted in terms of a mixture of oxidized states. Some of these states could be associated with Ti-C bonds that exist after 120s of sputtering as revealed by the C1s spectra. The O1s XPS spectra (not shown) taken from the surface show several peaks, some of which come from the adsorbed oxygen at the surface
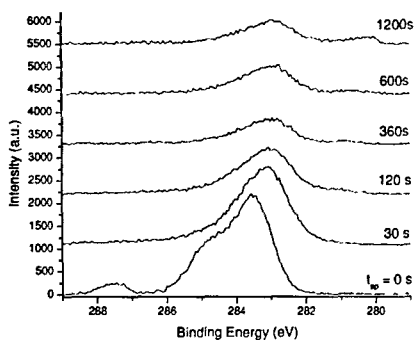

Figure 2a. XPS C 1s spectra from the "glass side" as a function of Ar-ion sputter time.
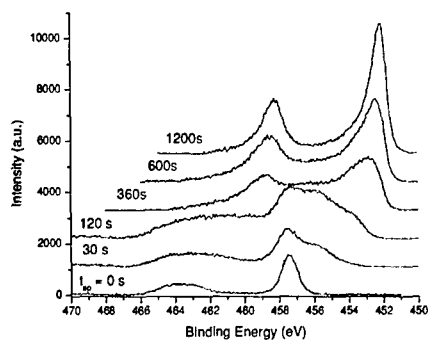
Figure 2b. XPS Ti 2p spectra from the "glass side" as a function of Ar-ion sputter time.

and some from the TiO_2 and the PI. Upon sputtering the adsorbed oxygen line disappears and only oxygen engaged in various Ti oxides is observed in agreement with what was described above for the C1s and Ti 2p XPS line cases.

Micro-Raman spectroscopy results

Typical Raman spectra of the BSG surface in the laser joint failure regions of as-received samples and 3-month CSF soaked ($37^{\circ}C$) samples are shown in Figures 3a and 3b, respectively. The baseline of the shown spectra was subtracted and then they were normalized to the intensity of the strongest peak. Also shown in these figures (bottom) is the spectrum of the original bulk BSG (Corning Pyrex 7740) taken under identical conditions. The second spectrum in each graph is taken from the exposed glass surface of the glass plate side of the failed (during a tensile mechanical strength measurement) joint sample. The top spectra in the graphs are taken from the exposed surface of glass fragments that were found on the PI side of the failed sample. These fragments represent regions of the laser joint where the joint failed in the glass volume and not at the very interface or in the PI volume. In these fragments the PI/Ti interface is preserved and is covered with (a thin layer of) glass, the spectrum of which is shown in the topmost position in each graph in Figure 3.

As it can be seen from Figure 3a, the glass side spectrum is almost identical to the one of the original glass. On the other hand, the spectrum from the PI side (top) shows some differences and these are indicated by arrows in the graph. The weak band around $1600cm^{-1}$ is almost absent in the PI side spectrum and so is the very sharp peak at $1410cm^{-1}$ while the peak at $1180cm^{-1}$ has considerably lower intensity. *These differences in the spectra indicate changes in the molecular structure of the glass in the glass fragments with respect to the original bulk glass.* If the structure of the glass is altered locally and/or defects are introduced it can be expected the glass will become weaker in the affected region and that region would be the one to fail in a mechanical strength test. The glass fragments on the PI side represent such altered/weakened *of the laser joint fabrication process (i.e. to the heat from fiber laser beam).*

The spectra of the 3-month CSF soaked laser joint samples (Figure 3b) are similar to those of the as-received ones and *show very few additional differences with respect to the original glass.* The PI side spectrum shows all the differences that are observed in the spectrum of the as-
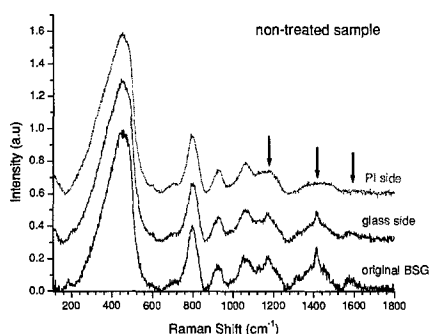

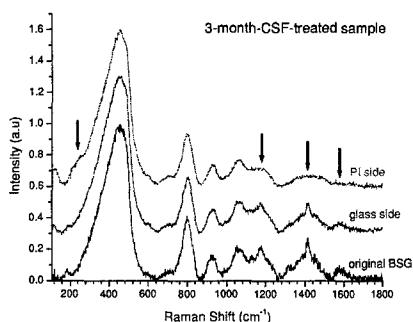**Figure 3a**. Raman spectra of BSG in the laser joint region of as-received samples

Figure 3b. Raman spectra of BSG in the laser joint region of 3-month CSF-soaked samples

received PI side. The only new change here is the weak elbow at about $250cm^{-1}$ that accompanies the main band at $450cm^{-1}$. The origin of this feature is not clear to us at this time.

As it became evident from the mechanical tensile testing and optical microscopy studies, after exposure to CSF the laser joints failure occurs predominantly in the PI. Therefore, Raman spectra of the PI surfaces (just CSF-treated, as-received laser joint region and a combination of both) could, in principle, provide further insight into the reasons for the partial mechanical weakening of the laser joints as result of exposure to CSF. Attempts at obtaining spectra of PI with our existing Raman facility have had little success due to strong fluorescence from the PI that obscures any Raman scattering signal. Other excitation sources should be helpful in overcoming this problem.

CONCLUSIONS

Biocompatible joints between polyimide and titanium-coated borosilicate glass with good long-term stability in physiological solutions and sub-millimeter width were fabricated by a novel laser technique. XPS characterization of such joints gave evidence for the formation of strong chemical bonds between Ti-containing species and certain polymeric functional groups. Raman spectroscopy results revealed some changes in the molecular structure of the borosilicate glass as a result of the laser fabrication process. These changes can be correlated with a general weakening of the glass in the joint region which is responsible for the failure of untreated laser joint samples upon tensile mechanical testing. The Raman results did not show significant changes in the glass as a result of a 3-month CSF soak. Based on these Raman results and optical microscopy inspection of the laser joints, the observed, limited joint strength degradation in CSF solution can be attributed mainly to weakening of the polyimide part of the laser joint interface.

ACKNOWLEDGEMENTS

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